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METHOD FOR MEASURING THE pH OF LEATHER USING A SIMPLE GLASS-ELECTRODE ASSEMBLY

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ABSTRACT

The glass electrode has been shown to function under conditions which are not favorable to either the hydrogen or quinhydrone electrode. Glass electrodes are now available which may be used in place of the hydrogen electrode, in the conventional potentiometric system, by substituting a galvanometer of high sensitivity and suitable characteristics in the electrical circuit. In view of the general use of pH measurements in specification and control work in the leather industry, a method which is rapid and accurate is desirable. A study has therefore been made of a simple glass-electrode assembly for measuring the pH value of leather extracts and tannin solutions. A method is proposed and the details of operation noted which are essential for accurate routine pH measurements. The Kerridge method of converting the emf readings of the glass electrode to corresponding pH units is described.

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I. INTRODUCTION

Kohn and Creede,¹ in 1923, suggested making pH measurements of water solutions in equilibrium with finely divided leather and plotting neutralization curves for a sufficient number of leathers of known tannage and wearing quality so as to establish a permissible upper limit for acidity. All the leathers which they considered good had an initial pH of practically 3 or higher. Since that time many other workers² have devised methods which involve the measurement of the pH of leather-water systems.

While interest in the possibility of using pH as a means of evaluating leather with respect to acidity has been increasing, the practical application of the method has made slow progress. The chief reason for this has been lack of confirmatory experimental data, correlating pH and the deterioration of leather as influenced by acid content, the kind of tanning materials used, and storage conditions.

Results of research are now available,³ however, which show the correlation between the initial pH values of different leathers and their

¹ J. Am. Leather Chem. Assn. 18, 189 (1923).

² See BS J. Research 10, 560 (1933) RP547 for list of references.

³ J. Am. Leather Chem. Assn. 28, 125 (1933); 29, 623 (1934); 30, 91 (1935).

deterioration in storage. These data serve as a valuable guide in selecting safe pH limits for vegetable-tanned leather.

The increased knowledge of the significance of the pH of leather will logically lead to its greater use in specifications and control work. This necessarily requires that the method for measuring pH be standardized. Equipment for this purpose has generally included the hydrogen electrode or in some cases the quinhydrone electrode. The latter has been shown to give erratic results in solutions containing tannin.⁴ The hydrogen electrode is susceptible to poisoning by many of the materials present in leather, and usually not more than two or three reliable readings can be obtained without renewing the coating on the platinum foil. The glass electrode has been shown⁵ to function satisfactorily with leather extracts and other solutions under conditions unfavorable to the use of either the hydrogen or the quinhydrone electrode or of indicators. Recently glass bulbs of low resistance have been made available, which may be used in the conventional potentiometric systems by substituting a galvanometer of high sensitivity and suitable characteristics in the electrical circuit. This development offers an assembly for use in making pH measurements which gives rapid and reliable results.

This report describes the glass-electrode assembly used, the essential details of operation which were followed, and the experimental work incident to the development of a method for measuring the pH of leather and tannin extracts.

II. EQUIPMENT

The apparatus used in this study is shown in figure 1. The potentiometer is a portable type calibrated to ± 0.5 millivolt. The galvanometer has a sensitivity of 0.0005 microampere, a 6-second period and a critical-damping resistance of 10,000 ohms. The reference half cell is a saturated potassium-chloride-calomel electrode, with side arm for dipping into the test solution and a dropping funnel inserted in the top for flushing after each determination. The half cell was placed in a dewar flask for protection against sudden changes of temperature. The glass electrode is of the bulb type having an internal reference electrode.

The glass electrode was insulated by supporting it from a bakelite rod. Shielding and grounding were found necessary, particularly during humid weather. The wires leading to the galvanometer were shielded with grounded metal cables and the galvanometer was shielded by a grounded copper case. The potentiometer rested on a grounded copper shield. Where possible the reading lamp should be lighted by alternating current, using a small transformer, since the use of direct current often causes induced currents which may affect the stability of the galvanometer coil.

III. STANDARDIZATION

Two glass electrodes having similar internal reference cells will not necessarily give the same emf readings in a standard buffer solution. This is caused by a difference in potential between the inner and outer surfaces of the glass, known as the "asymmetry potential" of the glass membrane.

⁴ BS J. Research 4, 737 (1930) RP176.

⁵ Burton and Acree, Ind. Eng. Chem. 6, 79 (1934).

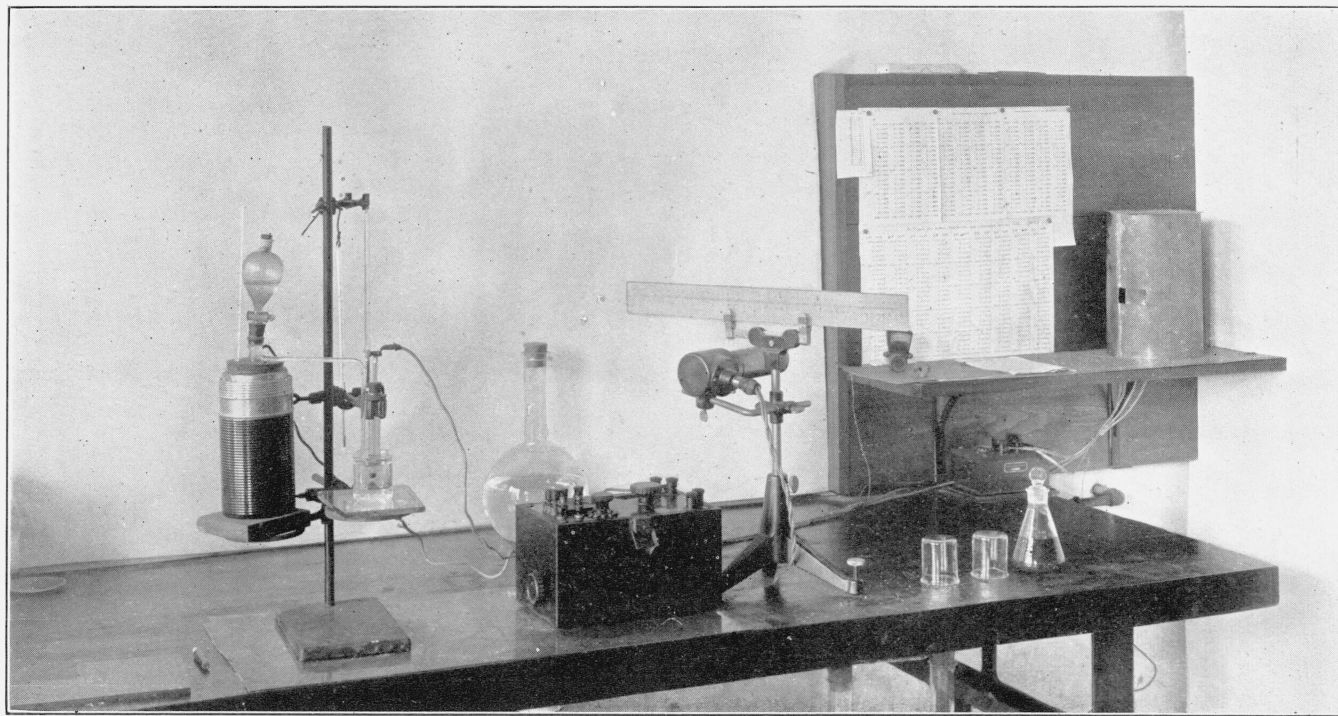


FIGURE 1.—Apparatus used for making pH measurements with the glass electrode.

This potential is not constant, but the change is usually very gradual over a period of weeks. Different electrodes may have slightly different characteristics, and for this reason the glass electrode should be considered as a secondary electrode which must be calibrated against the standard hydrogen electrode.

Since the glass electrode must be frequently calibrated, prepared tables for converting emf readings into corresponding pH units can be used only after a correction factor has been applied.

When the observed emf of a glass electrode is plotted graphically against the known pH of several buffer solutions, a straight-line graph, figure 2, should be obtained. This line will have a slope of 0.0591 volt per pH unit at 25°C within the range of 1 to 10 pH. Therefore,

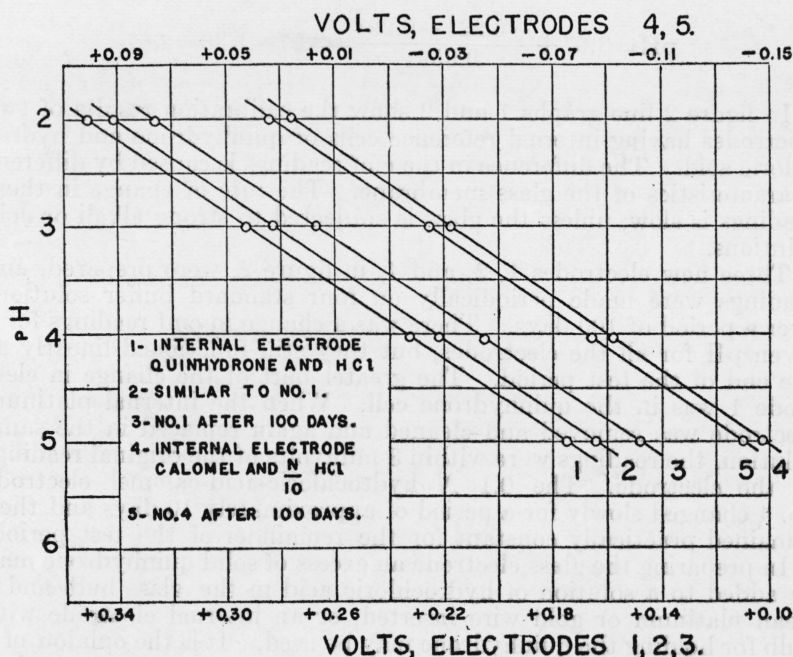


FIGURE 2.—Calibration graphs for glass electrodes with four buffers, versus saturated potassium-chloride-calomel electrode at 25° C.

for routine work it is usually sufficient to check the electrode against a standard buffer solution, having a pH near the working range desired.

The following formula for converting emf readings into corresponding pH units, described by Kerridge,⁶ is simple, eliminates any necessity for separate computation of the corrections in the readings, and applies to any internal reference cell.

$$\text{pH}_x = \text{pH}_b + \frac{E_b - E_x}{K},$$

where x = the unknown solution, b = the standard buffer solution used for calibration, and $K = (0.00019832) (273.1 + t)$, where t = tem-

⁶ J. Sci. Instr., 3 404 (1926).

perature in degrees C. The equation is given in algebraic form and emf readings must be inserted with proper signs. The sign given the glass electrode in this report is taken as the sign⁷ on the outer metallic terminal of the electrode, and is the same as that of the potentiometer binding post to which the glass electrode is attached at balance. This is the convention accepted by the National Bureau of Standards.

The following calculation is typical. If the observed emf reading at 25° C of a buffer solution (pH 3.97) with the glass electrode *versus* the saturated potassium-chloride-calomel electrode was found to be +0.221 volt and the observed emf of an unknown solution was +0.298 volt, then:

$$\text{pH} = 3.97 + \frac{+0.221 - 0.298}{0.0591} = 3.97 - 1.30 = 2.67$$

In figure 2 line graphs 1 and 2 show the calibration results of two electrodes having internal reference cells of quinhydrone and hydrochloric acid. The difference in the emf readings is caused by different characteristics of the glass membrane. The rate of change in these readings is slow, unless the glass is subjected to strong alkali or acid solutions.

Three new electrodes 1, 2, and 4, in figure 2, were prepared, and readings were made periodically on four standard buffer solutions over a period of 100 days. There was a change in emf readings for a given pH for all the electrodes, but they still functioned linearly at the end of the test period. The greater part of the change in electrode 1 was in the quinhydrone cell. When the internal platinum electrode was removed and cleaned and again replaced in the same solution, the readings were within 3 millivolts of the original readings of the electrode. The 0.1 *N* hydrochloric-acid-calomel electrode no. 4 changed slowly for a period of approximately 10 days and then remained practically constant for the remainder of the test period.

In preparing the glass electrode an excess of solid quinhydrone may be added to a solution of hydrochloric acid in the glass bulb and a clean platinum or gold wire inserted, or an internal electrode with bulb for holding the quinhydrone may be used. It is the opinion of a number of users of the glass electrode that the pH of the hydrochloric-acid solution used with the quinhydrone must be exactly 1, in order that tables furnished with some electrodes may be used for converting emf readings into pH units. This is not the case, since the emf of the glass electrode is practically independent of the pH of the hydrochloric-acid solution. This condition is caused by the fact that the potentials of the glass and quinhydrone electrodes are changed the same amount, whenever the pH of the internal hydrochloric-acid solution is changed. Any concentration of hydrochloric acid between normal and 0.1 normal is satisfactory for routine work.

In preparing a calomel internal reference electrode it must be provided with a bulb for holding the mercury and calomel in contact with the platinum wire. The emf of the glass electrode with an internal calomel electrode will vary with change in the pH of the internal hydrochloric-acid solution, because the glass acts as a hydrogen

⁷ Trans. Am. Electrochem. Soc. 36 3 (1919).

electrode while the mercury acts as a metal electrode. The solution usually used is 0.1 *N* hydrochloric acid.

The proper correction should be made in the conversion formula for the temperature at which the pH determinations are made with the glass electrode. The temperature of the solutions measured should be near that of the calomel reference electrode. A difference of 5° C will cause an error of approximately 0.06 pH unit.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

Since the method for measuring the pH of leather is empirical and is dependent upon the dilution of the extract (ratio of leather to water), it is necessary to establish a standard method, in order that work of different laboratories may be comparable. Kohn and Creede⁸ used a factor weight, 4.9 g of leather to 100 ml of water. This amount of leather was chosen for convenience in calculating titration data. Other investigators used varying amounts of leather and water.

It was found from experimental data on a large number and variety of leather samples that, when the ratio was between 4 and 6 g of leather to 100 ml of water, the extract was so well buffered that any variation between these limits caused no appreciable difference in the pH of the extract. A large amount of data had been collected in this laboratory and by others, using 4.9 g of leather to 100 ml of distilled water. In order that the accumulated data might be more closely correlated with future work, a ratio of 5 g of leather to 100 ml of water was selected.

In a committee report on the determination of acid in leather,⁹ the following items were studied with respect to their effect on the pH of the leather: (1) Method of preparing the sample; (2) filtering the leather extract; (3) grease content of the sample; (4) time of soaking, and (5) ratio of leather to water. The only factors found to have any appreciable influence on the pH were the time of soaking and the ratio of leather to water. The minimum time required for the sample to reach equilibrium with the water was found to be approximately 4 hours.

A comparison of the pH readings obtained with the glass and hydrogen electrodes in water extracts of leather has been made on a large number and variety of samples. Typical results are given in table 1, in which the pH values of 24 samples representing commercial and specially treated leathers measured with the hydrogen and glass electrodes, are shown.

TABLE 1.—pH measurements with glass and hydrogen electrodes in water extracts of leather

Sample	Glass	Hydrogen	Sample	Glass	Hydrogen	Sample	Glass	Hydrogen
1.....	5.25	5.08	9.....	2.75	2.74	17.....	4.64	4.61
2.....	2.66	2.66	10.....	2.73	2.76	18.....	3.03	3.04
3.....	3.57	3.47	11.....	2.76	2.76	19.....	2.54	2.50
4.....	2.28	2.25	12.....	2.75	2.72	20.....	3.97	3.97
5.....	3.19	3.21	13.....	2.76	2.77	21.....	4.50	4.50
6.....	3.19	3.18	14.....	3.19	3.21	22.....	2.48	2.49
7.....	3.19	3.18	15.....	3.34	3.35	23.....	2.64	2.67
8.....	2.75	2.74	16.....	2.97	2.98	24.....	3.59	3.54

⁸ J. Am. Leather Chem. Assn. 18, 189 (1923).

⁹ J. Am. Leather Chem. Assn. 29, 403 (1934).

It will be noted that the agreement was close with two exceptions. In sample 1 the hydrogen electrode was "poisoned" so rapidly that a steady reading could not be made, and in sample 3 copper plated out of the solution onto the hydrogen electrode.

In order to determine the effect of the tannins on the pH of leather, the pH-titration curves shown in figure 3 were made with the glass electrode in a sulphuric-acid solution and in solutions of sulphuric acid of the same strength containing commercial tannin extract. In the pH range between 3 and 4, where it has been shown that leather is unharmed by the acidity, the type or amount of tannin has little effect on the pH. Above pH 4 there is a large difference in the buffering effects of quebracho and chestnut tannin extracts. This indicates that the water-soluble tannins extracted from the leather

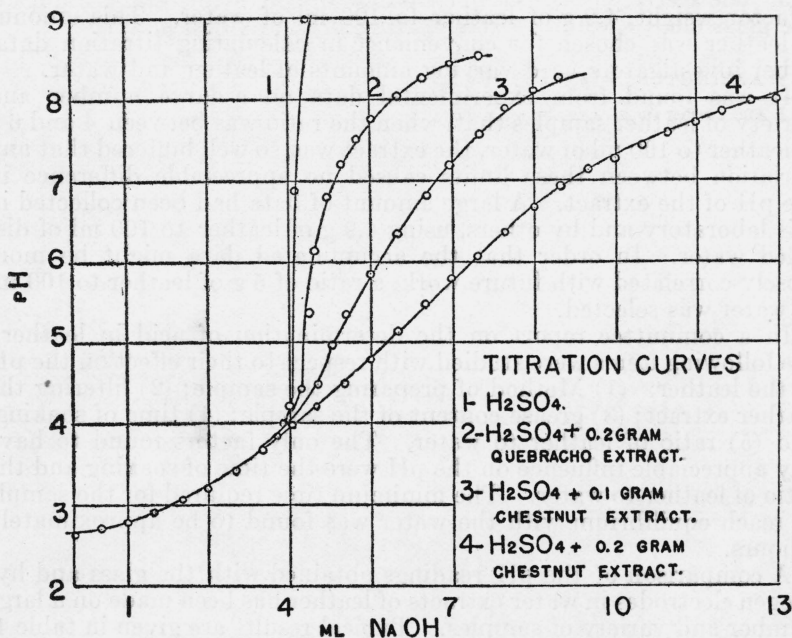


FIGURE 3.—Titration curves for sulphuric-acid solution and for sulphuric-acid solutions of the same strength containing tannin.

have no effect on the acidity within the normal range of a routine pH determination.

The effect of the temperature of the water used for extracting the leather, on the pH of the extract was determined as follows. Two leathers were used. One was tanned in the laboratory and treated with sulphuric acid and the other was a commercial sole leather. Distilled water (100 ml) at 25° C was added to 5-g portions of the leathers, as prepared for analysis, in glass-stoppered flasks.

One series was allowed to come to equilibrium at 10° C, one at 45° C, and the other maintained at 25° C. After 24 hours the solutions were filtered and pH determinations made at 25° C. The maximum variation in the samples was only 0.03 pH.

V. SUMMARY

1. From the results of this work it is recommended that the procedure for determining the pH value of leather proposed in the report of the committee on the determination of acid in leather ¹⁰ be revised to permit only the use of the glass electrode. The method should read as follows: Weigh 5 g of leather, as prepared for analysis, into a flask, add 100 ml of distilled water and stopper the flask tightly. Agitate the mixture immediately and allow it to stand for 4 hours. Again agitate the mixture and allow it to settle for 10 minutes, and determine the pH of the decanted extract with the glass electrode.

2. The glass electrode was found to be more rapid and to require less attention than the hydrogen electrode.

3. The Kerridge substitution method of converting emf readings of the glass electrode into corresponding pH units is described.

WASHINGTON, May 10, 1935.

¹⁰ J. Am. Leather Chem. Assn. **29**, 403 (1934).